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TECHNICAL REPORT 8901

ORGANIC EXPLOSIVES AND RELATED COMPOUNDS:
ENVIRONMENTAL AND HEALTH CONSIDERATIONS

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<p>This report is a compendium of a large body of information currently available in the open literature and in government publications on organic compounds used as explosives and in propellant formulations. While a summary of synthetic processes is included, emphasis is focused on behavior and fate of these compounds in the environment and their biological effects and potential for animal and human health concerns. Physicochemical properties likely to be of value in making environmental calculations and decisions are also listed and discussed.</p>					
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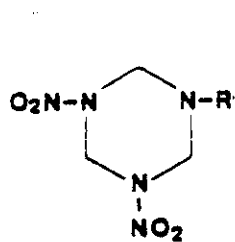
INTRODUCTION

Explosives and propellants have important military applications; the former are also widely used in mining and construction. Their manufacture represents a sizable segment of the chemical industry [1]. In the course of production, handling, loading of military or civilian devices, and ultimate dispersal or disposal, explosives and propellants are released to the environment. There they are disseminated by natural processes and partially converted to secondary products. This report deals only with the more important organic explosives and propellants, and the focus is primarily on physicochemical properties and behavior, environmental fate, toxicity to human beings and wildlife, and environmental criteria; a comprehensive review that emphasizes manufacturing processes, formulations and uses is available [2]. While reasonable attempts have been made to assemble all pertinent material, some sources will doubtless have been missed. In addition to such omissions, there are extensive gaps in our knowledge, especially of environmental fate and chronic toxicity. Table 1 is a summary of the compounds to be covered and the abbreviated names for them that will be used throughout the report.

Table 1. Listing of Explosives, Propellants, and Derived Substances

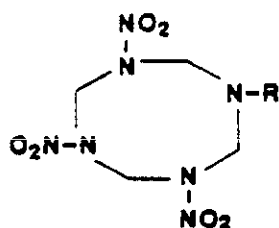
<u>Compound^a</u>	<u>Abbreviation</u>
Trinitrotoluene ^b	TNT
Dinitrotoluene ^c	DNT
1,3,5-Trinitrobenzene	TNB
1,3-Dinitrobenzene	DNB
Hexahydro-1,3,5-trinitro-1,3,5-triazine	RDX
Octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine	HMX
1-Acetylhexahydro-3,5-dinitro-1,3,5-triazine	TAX
1-Acetyloctahydro-3,5,7-trinitro-1,3,5,7-tetrazocine	SEX
N,2,4,6-Tetranitro-N-methylaniline	Tetryl
Ammonium picrate/Picric acid	AP/PA
Pentaerythritol tetranitrate	PETN
Nitroglycerin (glyceryl trinitrate)	NG
Nitroguanidine	NQ
Ethylene glycol dinitrate	EGDN
Diethylene glycol dinitrate	DEGDN
Propylene glycol dinitrate	PGDN

- Structures are presented in Figure 1.
- Where TNT is used, the 2,4,6-isomer (formerly known as α -TNT) is denoted; other isomers are specifically designated, e.g. 2,3,4-TNT.
- Where DNT is used, the 2,4-isomer is denoted, possibly with minor amounts of other isomers -- especially the 2,6-isomer; other isomers are specifically designated, e.g. 2,3-DNT.



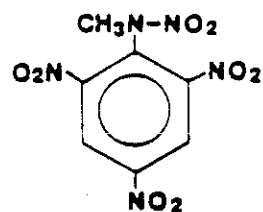
R=NO₂, RDX

R=Ac, TAX

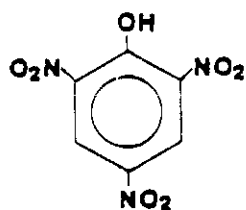


R=NO₂, HMX

R=Ac, SEX



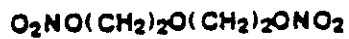
TETRYL



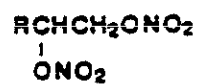
PA



NG



DEGDN



R=H, EGDN

R=CH₃, PGDN

R=CH₂ONO₂, NG



PETN

Figure 1. Structures of Explosives and Related Compounds

SYNTHESIS/PRODUCTION AND USE

Methods for the synthesis or industrial production and purification of the compounds of interest are summarized and referenced in Table 2. TNT, historically the most important and most widely used military high (or "secondary") explosive, has not been produced in the U.S. for several years. It is currently an important constituent, along with RDX (see below), of formulations known as Composition B. Crude TNT contained small amounts of the other five isomers which were converted by the "sellite" (i.e., sodium sulfite) process for TNT purification [3] to water-soluble dinitrotoluenesulfonate salts; the latter were destroyed by incineration of the "red water" concentrates in which they occurred. Thus, TNT isomers are ordinarily not observed as environmental pollutants. The dinitrotoluenes were present in TNT wastewaters and also in the purified product (military-grade TNT); 2,4-DNT is listed as a priority pollutant, and both 2,4- and 2,6-DNT have been detected as soil and groundwater contaminants. DNT is also utilized in its own right as a propellant constituent to control burning rates or to reduce hygroscopicity [4]. TNB is a stable end-product of TNT photolysis that occurs wherever TNT has been a soil surface contaminant or a water contaminant over a period of time [5]. DNB apparently arose through the nitration of benzene, present as an impurity of toluene, during the manufacture of TNT.

The most important military high explosive in the U.S. today is RDX (British code name for Research Department or Royal Demolition Explosive). It is formulated into munitions alone (Composition A) or as a slurry with molten TNT (Composition B). Production grade RDX generally contains significant amounts of HMX (code name for High Melting Explosive) as an acceptable impurity. By modification of the RDX synthetic process, HMX becomes the major product, with RDX as an impurity. HMX is being increasingly used, predominantly as a propellant and also in maximum-performance explosives. TAX and SEX are both common impurities and wastewater constituents associated with RDX/HMX manufacture.

Tetryl was formerly produced mainly as a booster explosive. It has not been produced in over a decade and has been superseded in this role by RDX.

Picric acid (PA) and especially its salt, ammonium picrate (AP), are reputedly rather insensitive to shock; they have been used as burster charges in naval projectiles.

PETN, employed in blasting caps and detonators, is easily initiated and exhibits highly reproducible responses.

Pure nitroglycerin (NG) is too sensitive and unstable for a practical high explosive. As an energetic plasticizer, the compound is added to nitrocellulose in blasting gelatins and is a component of most double-base and triple-base propellants. Glyceryl mono- and dinitrates (MNGs and DNGs) are found in the wastewaters of nitroglycerin manufacturing plants.

Nitroguanidine (NQ) is included in triple-base propellants to impart flashlessness and to reduce erosivity [6].

Table 2. Synthesis/production Processes and Purification of Explosives, Propellants, and Related Compounds

<u>Compound^a</u>	<u>Synthetic Process</u>	<u>Purification</u>	<u>References</u>
<u>INT^b</u>	Nitration of toluene	Isomer removal with aqueous sodium sulfite	[3,7]
<u>DNT^c</u>	Nitration of toluene	"Sweating" ^d	[4,8]
<u>2,4-DNT</u>	Nitration of 4-nitro-toluene	Recrystallization	[8]
<u>2,6-DNT</u>	Nitration of 2-nitro-toluene	Distillation	[4,8]
<u>TNB</u>	Decarboxylation of 2,4,6-trinitro-benzoic acid	Recrystallization	[9]
<u>DNB</u>	Nitration of benzene	Isomer removal with aqueous sodium sulfite	[10]
<u>RDX</u>	Nitrolysis of hexamethylenetetramine	Recrystallization	[11,12]
<u>HMX</u>	Nitrolysis of hexamethylenetetramine	Recrystallization	[13,14]
<u>TAX</u>	Nitrolysis of 1,3,5-triacetylhexahydro-1,3,5-triazine	Chromatography plus recrystallization	[15]
<u>SEX</u>	Nitrolysis of 1,5-diacetyloctahydro-3,7-dinitro-1,3,5,7-tetrazocine	Chromatography plus recrystallization	[16]
<u>Tetryl</u>	Nitration of N,N-dimethylaniline	Recrystallization	[17]
<u>NO</u>	Dehydration of guanidine nitrate	Recrystallization	[6]
<u>PA/AP^e</u>	Sulfonation, then nitration of phenol; ammoniation	Water washing	[18]
<u>PETN</u>	Nitration of pentaerythritol	Recrystallization	[19]

Table 2 (cont'd). Synthesis/production Processes and Purification of Explosives, Propellants and Related Compounds.

<u>Compound^a</u>	<u>Synthetic Process</u>	<u>Purification</u>	<u>References</u>
<u>NG^f</u>	Nitration of glycerol	Washing, drying	[20]
<u>EGDN</u>	Nitration of ethylene glycol	Probably washing	[21]
<u>DEGDN</u>	Nitration of diethylene glycol	Washing	[22]
<u>PGDN</u>	Nitration of propylene glycol	Probably washing	[23]

- a. Underlined compounds are the munitions compounds of primary interest; others are impurities or byproducts associated with the previously listed underlined compound.
- b. For syntheses of the isomers of 2,4,6-trinitrotoluene see references 24 and 25.
- c. For syntheses of the 2,3-, 2,5-, 3,4- and 3,5- isomers of DNT, see references 8, 24, and 26.
- d. "Sweating" of DNT [27] involves the gradual warming in a sieve-like "sweat pan" of a crystalline mixture of DNTs containing mostly the 2,4-isomer. The 2,6-isomer, along with minor constituents, forms a low-melting eutectic fraction that drains from the crystal mass through holes in the pan. The melting point of the residual material in the pan is thereby raised, as is the content of 2,4-DNT.
- e. Picramic acid, a metabolic product of picric acid, is prepared by the reaction of picric acid with sodium sulfide [28].
- f. For syntheses of the mono- and dinitrate esters of glycerol, see references 29, 30, 31, and 32.

EGDN is a liquid propellant component used in land mines to eject small projectiles upward to bursting heights.

DEGDN is more stable and less shock-sensitive than NG. It has replaced NG as a propellant plasticizer for some munition items.

PGDN is a component of "Otto fuel", a liquid naval torpedo propellant composed of 76% PGDN, 22.5% di-n-butyl sebacate, and 1.5% 2-nitrodiphenylamine [33].

PROPERTIES AND ESTIMATION METHODS

In this review, the only properties presented are those likely to be of value in making environmental calculations and decisions. For such use-related characteristics as detonation velocity and thermodynamics, the reader is referred to Lindner's article in the Encyclopedia of Chemical Technology [2].

The vapor pressure of a compound is commonly given for the state, solid or liquid, in which the substance is likely to occur under ambient conditions, typically 25°C. If the vapor pressure has been evaluated for a range of temperatures, the data may be presented as the constants of the Clausius-Clapeyron equation, $\log P = A - B/T$, where T is in degrees Kelvin (K). Table 3 gives values of A and B (pressure in torr) for the compounds of interest (except for AP, TAX and SEX). For a compound that is solid at ambient temperature, calculation of the Henry's Law constant, K_H , may require that the vapor pressure of the supercooled liquid be converted to the vapor pressure of the solid. The logarithm of the required conversion factor may be calculated by the equation

$$\log_{10} \{P(s)/P(l)\} = (\Delta S_f/2.303R)(T-T_m)/T, \quad (1)$$

where $R = 1.987$ cal/mole K, ΔS_f (entropy of fusion) is in the same units, and T is in degrees K [34]. When ΔS_f is not known, a value of 13.5 cal/mole K may be assumed for rigid molecules (whose definition for the present purposes includes all the solids discussed here) [35]. For the calculation at 25°C (298.16 K), the equation reduces to

$$\log_{10} \{P(s)/P(l)\} = 0.00989[25-T_m(^{\circ}\text{C})]. \quad (2)$$

When the heat of fusion, ΔH_m (after conversion into cal/mole), is known in addition to the melting point (T_m), one should use the relationship $\Delta S_f = \Delta H_m/T_m$ to obtain the entropy of fusion; this relationship depends on the fact that the free energies of the solid and liquid phases are identical at the melting point, so that ΔF_f (the free energy change in going from the solid to the liquid state) at that temperature is zero.

Solubilities of the munitions compounds at 25°C are given in Table 4; some of these values represent limited interpolations from those found in the literature. Aqueous solubilities at temperatures other than 25°C have been recorded for many of the compounds of interest by Lindner [2], Urbanski [6, 17-19, 36, 37], Fedoroff and Sheffield [38, 39], Kaye [4], Roth [40], and Spanggard et al. [5]. Where no solubility is available, it may be estimated from other properties, such as the octanol-water partition coefficient (K_{ow}), or from structural information [41]. Banerjee et al. [42] demonstrated, using RDX as an example, that the correlation of solubility with K_{ow} is considerably improved if the entropy of fusion is taken into account; this compensates for the fact that high-melting compounds are generally less soluble than liquids or low-melting compounds of otherwise similar properties. Their equation (applicable at 25°C) treats liquids as if they melted at 25°C:

$$\log K_{ow} = 6.5 - 0.89 \log S (\mu\text{mol/L}) - 0.015 t_m(^{\circ}\text{C}) \quad (3)$$

Table 3. Constants for the Clausius-Clapeyron Vapor Pressure Equation^a

Compound	A ^b	B	Reference
TNT	14.53;(12.31±0.34)	5900;(5175±105)	[43;(44)]
2,4-DNT	13.08±0.19	4992±59	[44]
2,6-DNT	13.99±0.18	5139±52	[44]
DNB ^c	8.56	3170	[45]
TNB	13.29	5608	[43]
RDX	15.12;(11.87)	7011;(5850)	[43;(46)]
HMX	14.72	8407	[43]
Tetryl	15.19	6987	[43]
PA	12.28	5488	[43]
PETN	18.08	7856	[43]
NG ^d	9.20±1.30	3525±399	[47]
NQ	14.15	7452	[43]
EGDN	10.55±0.08;(11.69±0.52) ^d	3476±22;(3830±159) ^d	[44;(47)]
DEGDN ^d	9.97±0.56	3637±17	[47]
PGDN ^d	10.19±0.30	3338±93	[47]

- a. $\log_{10} P$ (torr) = A - B/T (K). Indicated uncertainties are standard errors.
- b. Values of A in reference 43 were converted from units of $\log \text{Nm}^{-2}$ (Newtons per square meter, or Pascal) to torr by subtracting 2.125 (i.e., $\log 133.3$).
- c. The equation for DNB is for the supercooled liquid. The value of the vapor pressure at 25°C would be obtained by use of the liquid-to-solid state conversion factor presented in the text.
- d. Values of A and B were derived from vapor pressures presented in the reference for 15, 25, 35, 45 and 55° C.

or, rearranged,

$$\log S (\mu\text{mol/L}) = 7.30 - 1.12 \log K_{ow} - 0.0169 t_m (^{\circ}\text{C}) \quad (4)$$

The Henry's Law constant, K_H (or H), is often expressed in terms of (atmospheres·cubic meters)/mole; it is a measure of the ratio of concentration in the gaseous state to the concentration in solution (here restricted to aqueous solution). In the case of a substance that is appreciably dissociated (or associated) to ionic species, only the concentration of the uncharged species is relevant. Thus, PA is highly dissociated, with a pK_a of 0.38 [48], so that only 0.000025% remains as the undissociated molecule at pH 7; essentially, then, dilute picric acid in groundwater should have no vapor pressure. For Table 4, the following equation was used to calculate K_H from the vapor pressure (torr or mm of mercury), molecular weight, and solubility (mg/L):

$$K_H (\text{atm}\cdot\text{m}^3/\text{mol}) = (P \times \text{MW}) / (S \times 760) \quad (5)$$

If K_H is expressed in torr M^{-1} , it may be converted to (atmospheres·cubic meters)/mole through division by 760,000; K_H at 25 $^{\circ}$ C in (atmospheres·cubic meters)/mole can be converted to the dimensionless form through multiplication by the constant 40.88 mole/($\text{m}^3\cdot\text{atm}$).

Octanol-water partition coefficients are usually given in the logarithmic form, $\log K_{ow}$ (or $\log P_{ow}$). K_{ow} is defined as the ratio of a dissolved chemical's concentration in octanol (saturated with water) to its concentration in water (saturated with octanol) when the two liquid phases are at equilibrium, i.e., $K_{ow} = C_o/C_w$. For environmental purposes, K_{ow} is not employed in its own right, but frequently the starting point for estimating directly useful properties such as solubility, bioconcentration factors or soil organic carbon/water partition coefficient (K_{oc}) [49].

Experimental values for $\log K_{ow}$ of TNT determined independently in our laboratory [50] and another [51] are given in Table 4, and are in good agreement with the value calculated from experimental $\log K_{ow}$ values of 2,4-DNT or TNB through fragment substitution [52]. Experimental values have been published for three of the five nitrate esters considered here, NG, EDGN, and DEGDN (see Table 4). Values of $\log K_{ow}$ calculated for the five compounds using the π approach [52] are also included parenthetically, but are used for the estimations described below only in the cases of PETN and PGDN, where experimental data are lacking.

The soil organic carbon/water partition coefficient, K_{oc} , is defined as (μg adsorbed chemical per g organic carbon)/(μg chemical per mL of solution) [53]. Estimation of the actual partition coefficient, K_d , of a chemical between soil and water from K_{ow} is based on the assumption that the soil's organic content is the only determinant of the sorption of a compound from water to soil. Thus, $K_d = f_{oc} \times K_{oc}$, where f_{oc} is the fraction of organic carbon in the soil. The organic matter content may be converted to f_{oc} by multiplying it by 0.58 [53]. A number of equations have been developed to derive $\log K_{oc}$ from other environmentally relevant partition coefficients [53,54]. An example, which has been applied to a wide variety of organic solutes, is that of Lyman and Loreti [54]:

$$\log K_{oc} = 0.824 \log K_{ow} + 0.328. \quad (6)$$

BCF (fish), the water-to-aquatic organism (or simply "fish") bioconcentration factor, is defined as a concentration ratio determined at equilibrium (see reference 55), namely, chemical concentration in flesh (wet weight)/chemical concentration in water. In practice, many published determinations have been made under non-equilibrium conditions. Where experimental data or literature values were unavailable and estimates of BCF (fish) values were required for the present purposes, they were calculated from the octanol-water partition coefficients [56]:

$$\log \text{BCF} = 0.80 \log K_{ow} - 0.52. \quad (7)$$

For 2,4-DNT, an experimental value in bluegill striated muscle [57] was in good agreement with that calculated, and exceeded that estimated by the U.S. Environmental Protection Agency (EPA) [58] for edible fish flesh.

An equation for the bioconcentration factor, BCF (fat/feed, beef), based on the partitioning of chemicals between animal feed and the fat of the beef, was published by Kenaga in 1980 [59] and has been used for estimations in the present work (Table 4):

$$\log \text{BCF} = -3.457 + 0.500 \log K_{ow}. \quad (8)$$

In the same paper, Kenaga gave regressions based on water solubility, K_{oc} , and fish BCFs; he also presented regressions for fish BCFs and swine BCFs. These and other regression models were compared, evaluated, and extended to other mammals and poultry by Garten and Trabalka [60]. Most recently, Travis and Arms [61] have presented equations to relate $\log K_{ow}$ to "biotransfer factors" for organic chemicals in cattle (flesh and milk). They also presented a regression for vegetation bioconcentration based on $\log K_{ow}$.

While such equations have some usefulness in predicting bioaccumulation potential, substantial underestimations, especially for the less lipophilic compounds, may be expected if mechanisms unrelated to fat/water partitioning are important. As an example, for this report we utilized bioaccumulation data for RDX in rats (see metabolism section) and assumed a fat (lipid) content of 10% [62] in the rat to estimate a BCF (fat/feed) of 0.14, more than 100 times the Kenaga value for BCF (fat/feed, beef) (see Table 4). Such a comparison obviously ignores effects due to interspecies differences, but suggests that physicochemical regression models alone do not necessarily provide reliable estimates of bioaccumulation.

Table 4. Properties of Explosives, Propellants and Related Compounds

Property	Compound			
	TNT	2,4-DNT	2,6-DNT	TNB
CAS Reg. No.[63]	118-96-7	121-14-2	606-20-2	99-35-4
Empirical Formula	C ₇ H ₅ N ₃ O ₆	C ₇ H ₆ N ₂ O ₄	C ₇ H ₆ N ₂ O ₄	C ₆ H ₃ N ₃ O ₆
Molecular Weight	227.15	182.15	182.15	213.12
Density (g/cm ³)	1.65 [2]	1.521 [8]	1.538 [8]	1.63 [36]
Melting Point (°C)	80.75 [2]	72 [64]	66 [64]	122 [9]
Heat of Fusion (cal/g)	23.5[2]	26.1[8]	22.5[8]	16.0[65]
Vapor Pressure (torr, 25°C)	5.51x10 ^{-6a} (8.02x10 ⁻⁶ [44]) (3.7x10 ⁻⁶) ^b	2.17x10 ^{-4a}	5.67x10 ^{-4a}	3.03x10 ^{-6a}
Aqueous Solubility (mg/L, 25°C)	150[37]	280 ^c	206[50]	~385 ^d
K _H ^e (atm·m ³ /mole, 25°C)	1.10x10 ⁻⁸	1.86x10 ⁻⁷	~4.86x10 ⁻⁷	2.21x10 ⁻⁹
Diffusion Coefficient ^f (air)(cm ² /s)	0.064	0.067	0.067	0.068
Diffusion Coefficient ^g (water)(cm ² /s)	6.71x10 ⁻⁶	7.31x10 ⁻⁶	7.31x10 ⁻⁶	7.20x10 ⁻⁶
Log K _{ow}	2.00[50]; 1.86[51];(1.84) ^h	1.98[50,52]	1.89[50]; 2.02[51]	1.18[52]
Log K _{oc}	2.72[66]	2.40[66]	1.89 ⁱ	1.30 ⁱ
BCF (fish)	8.95 ^j	10.6[57]; 11.6 ^j ;3.8 ^k	9.82 ^j	2.65 ^j
BCF ^l (fat/feed, beef)	0.0029	0.0034	0.0031	0.0014

Table 4 (cont'd). Properties of Explosives, Propellants and Related Compounds

Property	Compound			
	1,3-DNB	RDX	HMX	Tetryl
CAS Reg. No.[63]	99-65-0	121-82-4	2691-41-0	479-45-8
Empirical Formula	C ₆ H ₄ N ₂ O ₄	C ₃ H ₆ N ₆ O ₆	C ₄ H ₈ N ₈ O ₈	C ₇ H ₅ N ₅ O ₈
Molecular Weight	168.12	222.15	296.20	287.17
Density (g/cm ³)	1.575[48]	1.83[2]	1.90(β form)[2]	1.73[2]
Melting Point (°C)	90[60]	205[42]	286[2]	129.5[2]
Heat of Fusion (cal/g)	28.97[67]	38.26[68] 32.86[69]	m	21.6[68]
Vapor Pressure ^a (torr, 25°C)	1.31x10 ⁻⁴	4.03x10 ⁻⁹	3.33x10 ⁻¹⁴	5.69x10 ⁻⁹
Aqueous Solu- bility (mg/L, 25°C)	533[70]	60[42]	5[71]	80[17]
K _H ^g (atm·m ³ /mole, 25°C)	5.44x10 ⁻⁸	1.96x10 ⁻¹¹	2.60x10 ⁻¹⁵	2.69x10 ⁻¹¹
Diffusion Coefficient ^f (air)(cm ² /s)	0.073	0.074	0.063	0.059
Diffusion Coefficient ^g (water)(cm ² /s)	7.94x10 ⁻⁶	7.15x10 ⁻⁶	6.02x10 ⁻⁶	5.99x10 ⁻⁶
Log K _{ow}	1.49[52]	0.87[42]; 0.81[50];0.86[51]	0.26[50]; 0.06[51]	1.65[51]
Log K _{oc}	1.56 ⁱ	2.00[66]	0.54 ⁱ	1.69 ⁱ
BCF ^j (fish)	4.70	1.50	0.49	6.31
BCF ^l (fat/feed, beef)	0.0019	0.00095	0.00047	0.0023

Table 4 (cont'd). Properties of Explosives, Propellants and Related Compounds

Property	Compound			
	PA	NQ	PETN	NG
CAS Reg. No.[63]	88-89-1	556-88-7	78-11-5	55-63-0
Empirical Formula	C ₆ H ₃ N ₃ O ₇	CH ₄ N ₄ O ₂	C ₅ H ₈ N ₄ O ₁₂	C ₃ H ₅ N ₃ O ₉
Molecular Weight	229.12	104.09	316.17	227.11
Density (g/cm ³)	1.76[2]	1.72[2]	1.78[2]	1.59[2]
Melting Point (°C)	123[2]	245(dec)[2]	141[2]	13.2[2]
Heat of Fusion (cal/g)	20[2]	m	76[2]	m
Vapor Pressure (torr, 25°C)	7.47x10 ^{-7a}	1.43x10 ^{-11a}	5.38x10 ^{-9a}	0.00177[47]
Aqueous Solubility (mg/L, 25°C)	12,400 ⁿ	4200[39]	2.1[72]	1950[73]
K _H ^e (atm·m ³ /mole, 25°C)	o	4.67x10 ⁻¹⁶	1.07x10 ⁻⁹	2.71x10 ⁻⁷
Diffusion Coefficient ^f (air)(cm ² /s)	0.066	0.102	0.057	0.070
Diffusion Coefficient ^g (water)(cm ² /s)	7.03x10 ⁻⁶	1.04x10 ⁻⁵	5.61x10 ⁻⁶	6.95x10 ⁻⁶
Log K _{ow}	2.03[52]	-0.83[74]	(3.71) ^p	1.62[75];1.77[51] (2.81) ^p
Log K _{oc}	2.00 ⁱ	-0.356 ⁱ	3.39 ⁱ	2.77[76];1.66 ⁱ
BCF (fish)	12.7 ^{j,q}	0.065 ^j	281 ^j	≤15[77]
BCF ^l (fat/feed, beef)	0.0036	0.00013	0.025	0.0023

Table 4 (cont'd). Properties of Explosives, Propellants and Related Compounds

Property	Compound		
	EGDN	DEGDN	PGDN
CAS Reg. No.[63]	628-96-6	693-21-0	6423-43-4
Empirical Formula	$C_2H_4N_2O_6$	$C_4H_8N_2O_7$	$C_3H_6N_2O_6$
Molecular Weight	152.08	196.14	166.11
Density (g/cm ³)	1.49[2]	1.38[2]	1.37[23]
Melting Point (°C)	-22.8[2]	-11.8[2]	<-20[23]
Heat of Fusion (cal/g)	m	m	m
Vapor Pressure (torr, 25°C)	0.0706[47]	0.00593[47]	0.0984[47]
Aqueous Solubility (mg/L, 25°C)	5600[38]	4000[2]	3500 ^r
K_H^e (atm·m ³ /mole, 25°C)	2.52×10^{-6}	3.83×10^{-7}	6.14×10^{-6}
Diffusion Coefficient ^f (air)(cm ² /s)	0.084	0.069	0.077
Diffusion Coefficient ^g (water)(cm ² /s)	8.72×10^{-6}	7.05×10^{-6}	7.93×10^{-6}
Log K _{ow}	1.16[75];(2.11) ^p	0.98[74];(1.13) ^p	(2.66) ^p
Log K _{oc}	1.28 ⁱ	2.03[74]	2.52 ⁱ
BCF ^j (fish)	2.6	1.84	40.6
BCF ^l (fat/feed, beef)	0.0013	0.0011	0.0075

- a. Vapor pressures were calculated from constants in Table 3 by use of the Clausius-Clapeyron equation. Note the correction required for DNB (footnote d to Table 3).
- b. The vapor pressure for TNT at 25°C was estimated by linear interpolation between data for 21.5 and 25.5° [78].
- c. The solubility of 2,4-DNT was estimated by linear interpolation between data

- for 22° and 50°C [4].
- d. The solubility of TNB was estimated by interpolation of a plot of $\ln S$ [36] vs. $1/T$ (K) for 17°, 50° and 100°C (i.e., 290, 323 and 373K).
 - e. K_H values were calculated from listed values of vapor pressure and solubility (equation 5).
 - f. Diffusion coefficients in air were estimated according to the FSG method described in chapter 17 of reference 49.
 - g. Diffusion coefficients in water were estimated according to the Hayduk-Laudie method (chapter 17 of reference 49), which requires judgement in the choice of some of the volume increments. A value of 20 for the 8-membered ring was used for HMX.
 - h. This value was calculated from $\log K_{ow}$ values for 2,4-DNT or TNB through fragment substitution [52].
 - i. Values of $\log K_{oc}$ were calculated by the equation of Lyman and Loreti [54] (equation 6).
 - j. Values of BCF (fish) were calculated from $\log K_{ow}$ by the equation of Isnard and Lambert [56] (equation 7).
 - k. This value was estimated by USEPA [58].
 - l. Values for BCF (fat/feed, beef) were estimated from $\log K_{ow}$ by the equation of Kenaga [59] (equation 8).
 - m. Information not available.
 - n. The solubility of PA at 25°C was estimated by linear interpolation between values for 20° and 30°C [18].
 - o. K_H was not calculated for PA, as explained in the text.
 - p. This value was calculated from π constants [52] (see text).
 - q. A value of <1 in trout epaxial muscle was found experimentally [79] (see metabolism section).
 - r. The solubility of PGDN was estimated from $\log K_{ow}$ according to equation 4 [42].
-

ANALYTICAL METHODS

A comprehensive review of this topic was published by Yinon in 1977 [80]. Therefore this section will highlight some of the more recent contributions and trends in the field.

The most versatile and probably the most widely used method for separating mixtures of nitroaromatics, nitramines, and nitrate esters in aqueous media is high pressure liquid chromatography (HPLC) on reverse phase columns. HPLC is readily coupled with chemical ionization mass spectrometry (CIMS) in positive (PCIMS) [81,82] and/or negative (NCIMS) [83,84] mode for identification, and with UV absorbance for quantitation [85-90]. Electrochemical detectors [91-94] and thermal energy analyzers (TEA)[95,96] have also been coupled with HPLC. For NQ, HPLC with quantitation by UV absorbance [97] or reductive electrochemical detection [98] is the method of choice.

Gas chromatography (GC) continues to be widely used for separation of mixtures containing the more volatile, thermally stable compounds, and is coupled to electron impact (EI) MS [99] or CIMS [99,100] for identification and to electron capture (EC) detectors for quantitation [101-104]. In one study, TEA was compared with EC for GC detection and was found preferable at low ng levels [105]. The use of macroreticular resins as an alternative to solvent extraction to remove and concentrate munitions compounds from groundwater samples prior to GC/EC analysis [106] or to HPLC analysis [94] has been described.

While numerous TLC protocols for munitions compounds have been published over several decades [80], new variations continue to appear. Some recent examples include two-dimensional TLC separations of multi-class components of explosives [107] and an improved procedure for nitrate esters and their metabolites and/or hydrolysis products [108].

The PCIMS of RDX [109] and the NCIMS of RDX, HMX, TNT, PETN, and NG [110] have been examined in detail and the fragmentation pathways discussed. PCIMS and NCIMS for DNT, PA, and tetryl [111], and field desorption (FD) MS of RDX, HMX, TNT, PETN, and NG, have also been reported [112].

Finally, tandem mass spectrometry (MS/MS) [113] constitutes a powerful new technique for the separation and characterization of mixtures. Picogram amounts of a desired analyte in a complex mixture can frequently be determined without prior GC or LC separation. The molecular ion or other prominent ion characteristic of the analyte is selected and its fragmentation pathway can be verified, without interference from other ions due to other components of the mixture. An investigation of the fragmentation pathways of TNT by high resolution EI MS/MS using ^{15}N and ^2H labeling revealed that the predominant processes are loss of OH followed by loss of NO or NO_2 [114]. These pathways were confirmed and studied in detail for a series of ten 2,4,6-trinitroaromatics [115]. A study of the high resolution MS/MS fragmentation pathways of RDX and HMX in EI, PCI, and NCI modes has also been published [116]. Additional MS/MS measurements in EI, PCI, and NCI modes have been reported for RDX, HMX, TNT, DNT, PETN, NG, EGDN, and PA [117]. An ion trap detector has recently been used for MS/MS measurements of TNT, DNT, 2,6-DNT, and RDX in NCI mode [118]. A review of the uses of mass spectrometry for detection and analysis of explosives in forensic chemistry has also been published recently [119].

ENVIRONMENTAL FATE

ENVIRONMENTAL ENTRY AND DISTRIBUTION

The major route of environmental entry for munitions compounds is the discharge of waste streams generated during their manufacture and processing to surface water. The levels in such wastewaters vary widely, depending on the intensity of the manufacturing operations and efficacy of the treatment technologies employed. For example, numerous surveys of effluent TNT levels at munitions plants have reported concentrations ranging from <0.05 mg/L to near saturation in the worst cases [120]. On the other hand, effluents at Holston Army Ammunition Plant, Kingsport, TN (HAAP), the only U.S. facility currently manufacturing RDX and HMX, did not vary greatly, and average yearly concentrations

of the nitramines were 2-6 mg/L [121]. Dilution of the effluent by the receiving surface water clearly reduces pollutant concentrations dramatically; reductions below detection limits are generally found one or two miles downstream [120].

In the manufacture of TNT, numerous nitroaromatic by-products are formed and enter the effluent as plant cleanup and scrubber wastes and as condensates from the evaporative concentration of "red waters" (i.e. settling wastes) [122]. Characterization of the steam-volatile trace organics of a representative TNT effluent led to the identification and quantitation of over 30 nitroaromatics. Repeated sampling over a one-year period showed that 2,4- and 2,6-DNT and 1,3-DNB were, in that order, consistently the major effluent constituents, and together represented approximately 75% by weight of the total volatile organics [123].

In the manufacture of RDX and HMX the by-products are TAX and SEX. Levels of TAX are reduced to below detection limits in HAAP effluents by conventional biological wastewater treatment [121]; RDX levels are reduced to a lesser extent, and levels of HMX and SEX are not substantially changed by this treatment.

Soil contamination by munitions compounds has occurred at open-burning and incinerator sites, and also can result from operational spills and seepage from landfills and wastewater holding facilities. Pollutant levels can be extremely high in wastewater lagoon beds, an example being a lagoon inactive for 20 years where TNT concentrations were as high as 3000 mg/kg [124]. Soil surveys of most other munitions plants indicate concentrations several orders of magnitude lower, even at disposal and open-burning sites. An example of the latter is sites where RDX concentrations reached 70-80 mg/kg [125].

An important consequence of the burden of munitions compounds in soils is contamination of ground water. Lysimeter studies have shown TNT migration to be slow in loamy and sandy soils; the somewhat more rapid movement in clay soils was attributed to channeling [126,127]. Nevertheless, a field study reported levels of TNT of >600 µg/L in shallow ground water owing to translocation from a munitions waste disposal bed [99]. In addition, smaller amounts of DNT and two microbial reduction products of TNT (see microbiological transformations section) were found. RDX was observed to migrate slowly in soils [126], but was also present at levels from <20 to >700 µg/L in ground water in the vicinity of contaminated sites.

PRINCIPAL ENVIRONMENTAL FATE PROCESSES

In general, two processes can significantly affect the fate and distribution of munitions pollutants in the environment: microbiological transformations and photochemical transformations. They will be discussed in the two following sections. Physical transport from aqueous systems is believed to be unimportant because both volatilities and sediment adsorption coefficients of the compounds are low (see Table 4). There is as yet no evidence for other important chemical transformation processes, such as hydrolysis or oxidation, under environmental conditions, with the possible exception of a very slow hydrolysis of tetryl (extrapolated $t_{1/2} = 302 \pm 76$ days at 20°, pH 6.8) [128].

MICROBIOLOGICAL TRANSFORMATIONS

Microorganisms capable of metabolizing TNT have been reported in soils, composts, muds, and fresh waters and their sediments, as well as in biological waste treatment systems [127,129-133]. Such transformations have been associated with species from numerous common aerobic and anaerobic bacterial genera including *Pseudomonas*, *Escherichia*, *Bacillus*, *Citrobacter*, *Enterobacter*, *Klebsiella*, *Veillonella*, and *Clostridium*. Fungal species representing 98 genera can also transform the compound [134].

While one case of a microorganism growing on TNT as a sole carbon source has been reported [135], the requirement of supplementary nutrients for the metabolism of TNT is now generally well-recognized. Biological systems with added domestic sewage and river sediments have resulted in significant TNT decreases [132,136], and laboratory cultures with added bacteriological media have resulted in rapid TNT disappearances of 100 mg/L or more [137,138]. In similar studies, incubation of activated sludge microorganisms with nutrients and ring-labeled ^{14}C TNT resulted in its complete disappearance without formation of labelled CO_2 (mineralization) [139]. Thus, it has been concluded that TNT undergoes bio-transformation but not biodegradation. The principal products observed from these microbiological transformations of TNT and pathways of their formation are shown in Figure 2. Successive reduction of the nitro groups to amino groups is believed to proceed through hydroxylamine intermediates (not isolated), of which the two shown can also couple to form the observed tetranitroazoxytoluenes [131]. Which products predominate depends on the nature of the microbial preparation, species of microorganisms involved, and conditions under which nitro group reduction takes place. Similar reductive transformations by thermophilic microorganisms under composting conditions were also observed [140]. In a later ^{14}C TNT composting study, however, only traces of reduction products were found; most of the label was associated with non-extractable humic-like materials [141]. Microbial action during treatment of a synthetic munitions-containing wastewater in a semi-continuous activated sludge system resulted in complete disappearance of TNT. Metabolites were sought at various stages of the treatment, and only at a very early stage was 4-amino-2,6-DNT found. It disappeared rapidly, and no other relevant aromatics were detected, but the study had not been designed to determine whether or not biodegradation had taken place [142].

Microorganisms also have the potential to metabolize many of the other nitroaromatic compounds found in TNT production wastewaters. DNT and DNB, unlike TNT, have been shown to be biodegradable. In each case a mixed culture was developed that could grow on and extensively degrade its respective substrate to CO_2 [76,143]. In similar experiments the more highly nitrogen-substituted wastewater constituents TNB and 3,5-dinitroaniline were not biodegradable [144]. Rather, the slow decreases in their concentrations occurring in the presence of river sediments were attributed to transformations not involving ring cleavage; in both cases amino compounds were formed. Biotransformation involving nitro group reduction has also been observed in the case of DNT, which under aerobic conditions gave rise to mixtures of amino- and azoxyaromatics analogous to the TNT reduction products shown in Figure 2 [145,146]. Under anaerobic conditions with an exogenous carbon source, the two unstable mononitroso isomers could also be isolated [147]. Little is known about rates of biotransformation of nitro-aromatics in the environment except that DNT and TNB, like TNT [124], have been

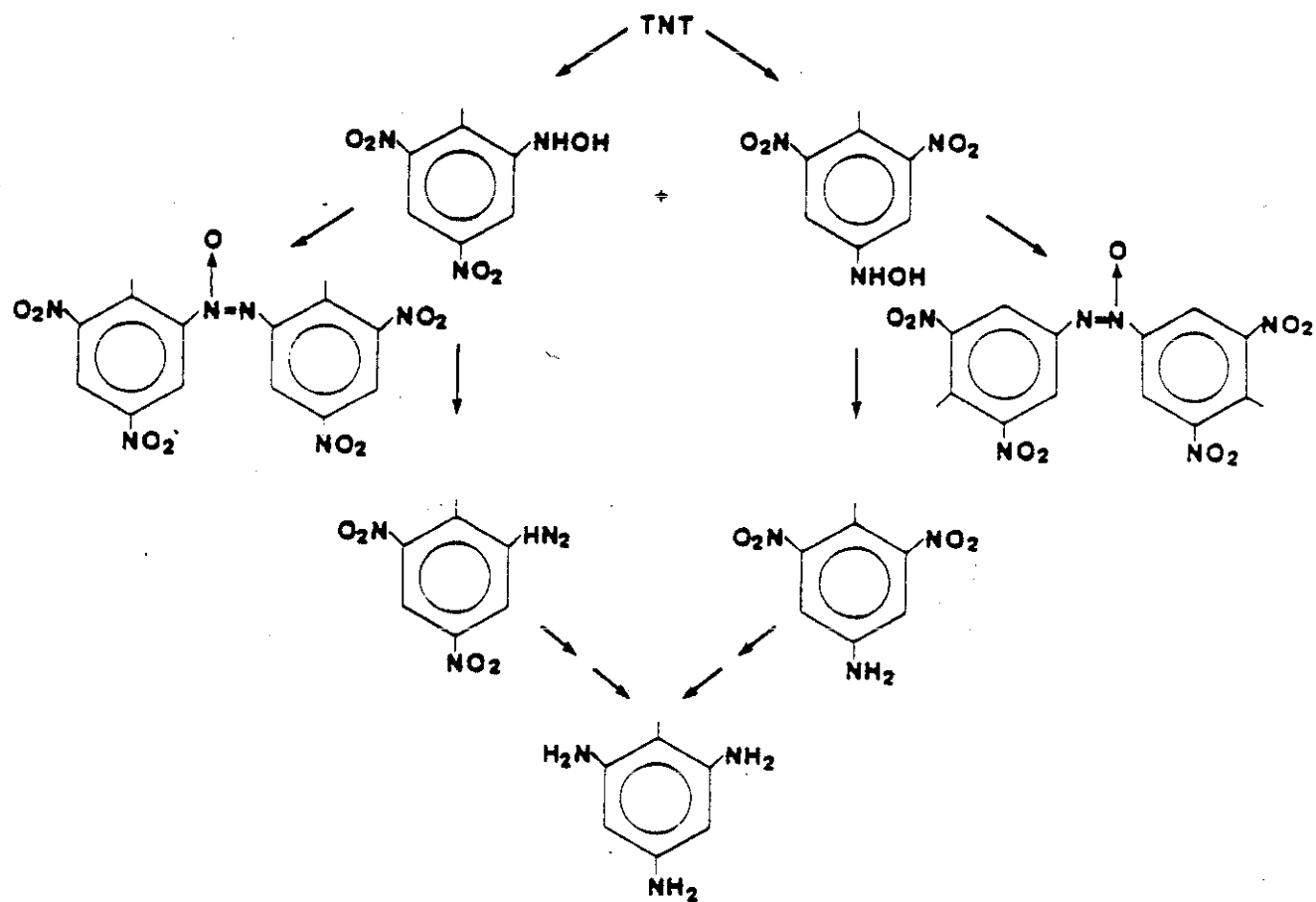


Figure 2. Microbiological Transformations of TNT

found to persist in soils and wastewater lagoon sediments for many years after a munitions facility became inactive [148,149].

Despite intensive effort by several groups of investigators, it must be concluded that aerobic biotransformation has little if any effect on the presence of RDX or HMX (or their congeners TAX and SEX) in the environment [76,150,151]. On the other hand, certain anaerobic sludge treatment systems with high supplemental nutrient levels were found to effect reductive transformations with relative rates $RDX > TAX > HMX > SEX$ [152-154]. Methanol, formaldehyde, hydrazine, 1,1-dimethylhydrazine, and 1,2-dimethylhydrazine were the major products; sequential pathways involving reduction to nitroso- and hydroxylaminonitramines followed by cleavage reactions were proposed to account for the transformations [152]. Thus, aerobic microorganisms in surface waters appear to be of no consequence in removing nitramines from the aquatic environment, and the significance of anaerobes in removing them from soils and standing water zones or bottom sediments of high nutrient content cannot be more than speculative.

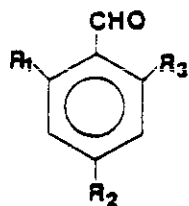
Similarly, NQ is not biotransformed aerobically. However, on prolonged anaerobic treatment of NQ with activated sewage sludge containing high levels of nutrient broth, partial or complete conversion to nitrosoguanidine (NSQ) took place. Small amounts of cyanamide, cyanoguanidine, melamine, and guanidine, which resulted from non-biological degradation reactions of NSQ, were also detected [155]. NQ was not biodegraded in soils except in the presence of high levels of supplemental glucose [156].

In contrast, NG and a number of other aliphatic nitrate esters commonly used in propellant formulations undergo aerobic biodegradation quite readily. Breakdown of NG was found to take place in stages via the isomeric di- and mononitrates, with each successive step proceeding at a slower rate [157]. PGDN, DEGDN, and TEGDN were each found to biodegrade through similar successive steps [158,159].

CHEMICAL TRANSFORMATIONS

Photochemical transformations, due to the effect of sunlight on munitions compounds in environmental waters, are more important than microbiological transformations because their rates are often significantly higher. Indeed, RDX, HMX, and NQ, which strongly resist biodegradation, are readily degraded photochemically. The photochemistry of munitions compounds (notably TNT, and to a lesser extent other nitroaromatics, RDX/HMX, and NQ) has been studied extensively in the laboratory, and because the results, with a few exceptions, have not been published in the open literature, we shall cover them in some detail.

The photolysis of TNT in dilute aqueous solutions, with a medium pressure mercury lamp and a pyrex filter to eliminate wavelengths below 280 nm, gave rise to complex mixtures, owing to further reaction of the primary photoproducts formed initially [160-162]. The major primary photoproduct, 2,4,6-trinitrobenzaldehyde (1a), was converted, presumably through the intermediate 2-nitroso-4,6-dinitrobenzoic acid, to the azoxydicarboxylic acid 2a, commonly referred to as the "white compound"; the latter is found as a byproduct in the production of TNT. Smaller amounts of azodicarboxylic acid 3 ("deoxy white compound"), decarboxylated azoxy compound 4, and amide 5 were also formed. In addition, the four isomeric

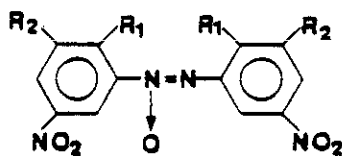


1a $R_1 = R_2 = R_3 = \text{NO}_2$

1b $R_1 = \text{NH}_2$, $R_2 = \text{NO}_2$, $R_3 = \text{H}$

1c $R_1 = R_2 = \text{NO}_2$, $R_3 = \text{H}$

1d $R_1 = R_3 = \text{NO}_2$, $R_2 = \text{H}$

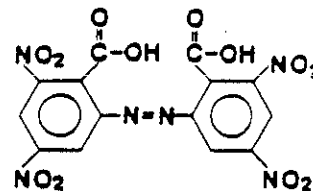


2a $R_1 = \text{CO}_2\text{H}$, $R_2 = \text{NO}_2$

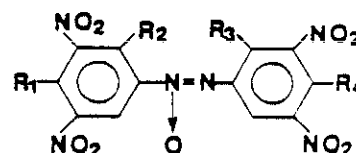
2b $R_1 = \text{CHO}$, $R_2 = \text{NO}_2$

2c $R_1 = \text{CO}_2\text{H}$, $R_2 = \text{H}$

2d $R_1 = \text{CHO}$, $R_2 = \text{H}$



3

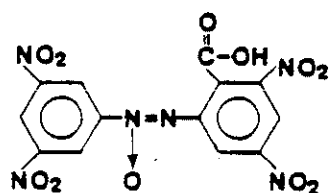


6a $R_1 = R_4 = \text{CH}_3$, $R_2 = R_3 = \text{H}$

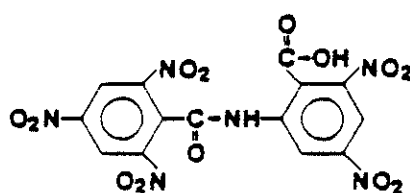
6b $R_1 = R_4 = \text{H}$, $R_2 = R_3 = \text{CH}_3$

6c $R_1 = R_3 = \text{H}$, $R_2 = R_4 = \text{CH}_3$

6d $R_1 = R_3 = \text{CH}_3$, $R_2 = R_4 = \text{H}$



4



5

Figure 3. Structures of Compounds 1-6

tetranitroazoxytoluenes 6a-d were present as minor products [160].

Two other important photoproducts were 2-amino-4,6-dinitrobenzoic acid (7a) and 4,6-dinitro-1,2-benzisoxazole (4,6-dinitroanthranil, 8a). The latter was photolabile and was converted on further irradiation to the tetracyclic compound 9. A minor photoproduct, 2,4,6-trinitrobenzyl alcohol, was also photolabile and gave rise to mixtures of aldehyde 1a, azoxydialdehyde 2b, and 3.

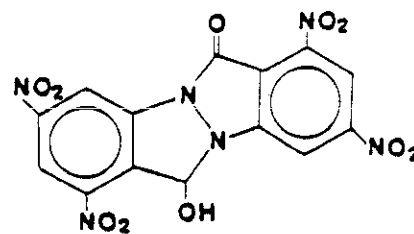
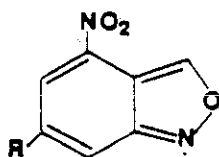
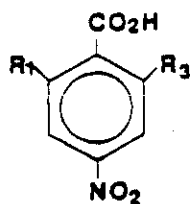
While 1a was also the principal sunlight-promoted TNT photoproduct in distilled water, TNB (a minor product in the laboratory studies) was the major photoproduct observed in a similar study of the effect of sunlight on TNT in natural river water [163]. This photostable compound then underwent slow biotransformation via nitro group reduction to 3,5-dinitroaniline.

Similar laboratory studies on other nitroaromatics have shown that photolysis of 2,4-DNT follows a similar course: the major products isolated were 2-amino-4-nitrobenzoic acid (7b), 2-amino-4-nitrobenzaldehyde (1b), and azoxydicarboxylic acid 2c; smaller amounts of 2,4-dinitrobenzaldehyde (1c), 2,4-dinitrobenzoic acid (7c, DNBA), and azoxydialdehyde 2d were present as well [161]. Photolysis of 2,6-DNT gave rise to unstable mixtures; little is known of the identities of the products except that 2,6-dinitrobenzaldehyde (1d) and 6-nitroanthranil (8b) were probably present, in addition to certain azoxy- and azobenzenes [161]. Evidence for the presence of oligomers of azoxy/azobenzenes (3 or more aromatic rings) was also found.

Photooxidation of 2,4-DNT in the presence of large excesses of hydrogen peroxide resulted in oxidation to the corresponding acid (via the alcohol and aldehyde), decarboxylation, and hydroxylation of the resulting DNB. Subsequent ring cleavage to mixtures of low molecular weight acids and aldehydes was observed [164].

As to the mechanism of phototransformation of TNT, the rate of disappearance of TNT was inversely proportional to pH, and in D₂O the deuterium content (found only in the methyl group) of the recovered TNT was substantially greater at the lower pHs [162,165]. Thus the reaction is believed to proceed by intramolecular hydrogen transfer in the triplet excited state to the aci-quinoid species 10, followed by deprotonation to the intermediate TNT anion 11, which can react further or reprotonate (Figure 5). Further evidence for the intermediacy of 11 was a trapping experiment with p-nitroso-N,N-dimethylaniline to form a Schiff base [165].

- Rate enhancements of 10 to 100-fold for TNT photolysis in natural waters have been observed and may be attributed to the action of humic acids as triplet sensitizers [166]. A study of 19 nitroaromatics under similar conditions showed enhancements of 2 to 26-fold, with the greatest in cases of nitro groups with ortho methyls. Thus, 2,6-DNT showed a greater enhancement than 2,4-DNT [167]. A recent investigation to probe the nature of excited species in humic-sensitized photoreactions of aquatic pollutants showed that the key steps in the reactions studied (photoisomerization of 1,3-pentadiene and photooxidation of 2,5-dimethylfuran) involved the transfer of electronic energy from triplet states of the humic substances, some sufficiently high to transfer energy to nitroaromatics [168].



9

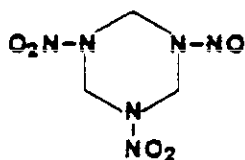
7a $R_1 = \text{NH}_2$ $R_2 = \text{H}$

8a $R = \text{NO}_2$

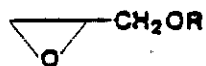
7b $R_1 = \text{NH}_2$ $R_2 = \text{H}$

8b $R = \text{H}$

7c $R_1 = \text{NO}_2$ $R_2 = \text{H}$



18



19a $R = \text{NO}_2$

19b $R = \text{H}$

Figure 4. Structures of Compounds 7-9, 18, 19

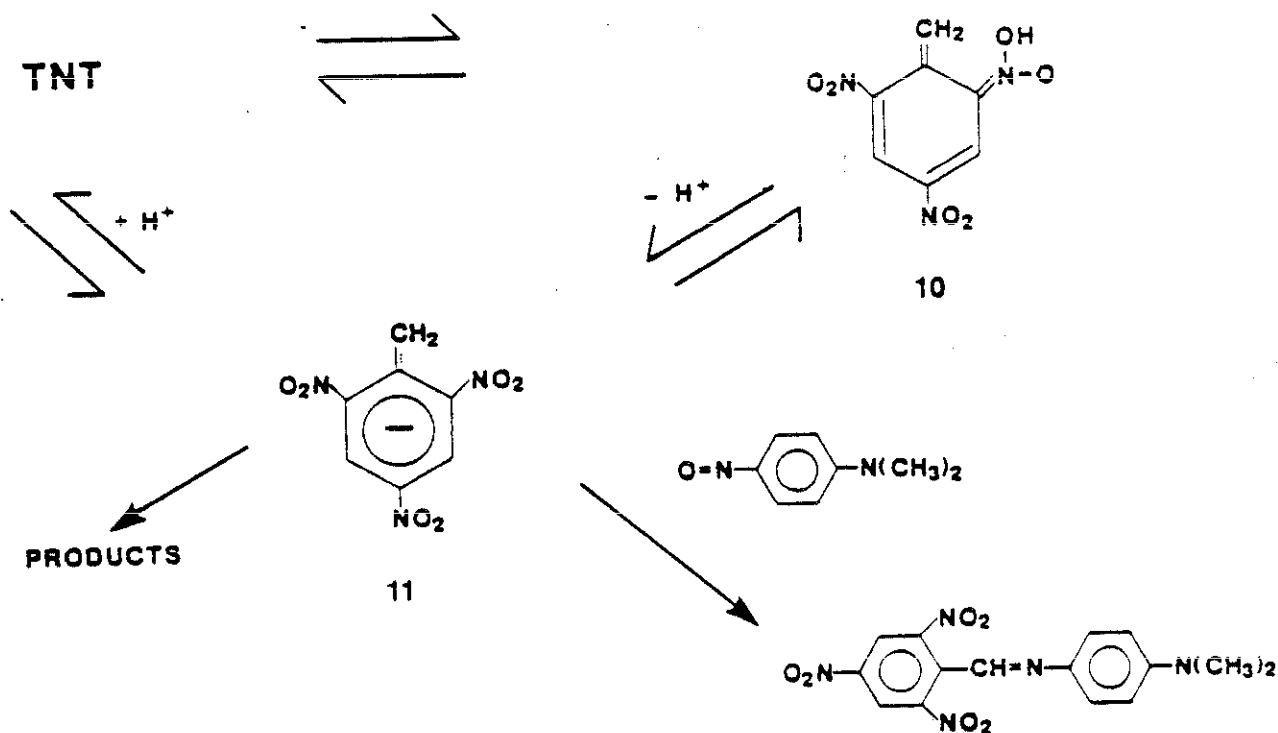


Figure 5. Mechanism of Photolysis of TNT

Laboratory studies have shown that UV photolysis of nitramine munitions in aqueous solutions with an unfiltered medium pressure mercury lamp is exceedingly facile (completion within 7-10 min), and the ultimate products are nitrate, nitrite, ammonia, and formaldehyde [169,170]. Carbon dioxide was formed only if the mixtures were treated with ozone during or after photolysis [170]. Photolysis alone has been viewed as a possible cost-effective small-scale alternative to activated carbon for removal of nitramine munitions from wastewater effluents [171]. Studies of the early stages of photolysis of RDX have led to the isolation and characterization of some of the intermediate organic nitro compounds, and have contributed substantially to our understanding of these complex photoprocesses [170,172,173]. The results, summarized in Figure 6, indicated that several different pathways may be operative. Photolysis in ethanol revealed one probable course of the reaction in water: in ethanol the products isolated were ethyl nitrate (12a), diethyl formal (13a), and methylenedinitramine (14) [172]. In water a similar pathway would lead to nitrate and formaldehyde (13b); 14 decomposes in water to formaldehyde and nitrous oxide, which have also been observed [173]. Three other products isolated from aqueous photolysis were assigned structures 15, 16, and 17 on the basis of their mass spectra, and were viewed as arising by a different pathway, possibly via a transient nitrodihydro-triazine [170]. Evidence for formation of the nitroso compound 18 was also found [173].

Aqueous solutions of both RDX and HMX were photolyzed slowly by sunlight to mixtures of the same ultimate products found in the UV laboratory study of RDX; rates observed were in terms of days rather than minutes, and RDX reacted 2-3 times faster than HMX [150].

Tetryl in aqueous solution was also photolyzed slowly by sunlight (20 days to essential completion); N-methylpicramide, nitrate, and nitrite were the major products [128]. A slower hydrolysis (90 days to essential completion) was observed at pH 9 in buffered solutions protected from light; the major products were methylnitramine and picrate ion [128].

NQ in aqueous solution was photolyzed even more readily by UV irradiation (254 nm) than RDX, and the rates of photodegradation by sunlight in natural waters were comparable to RDX [74,174]. Laboratory studies of the UV photolysis of NQ, summarized in Table 5, showed the products to be primarily guanidine, urea, and nitrite, with lesser quantities of cyanoguanidine, ammonia, and nitrate. Nitrosoguanidine (NSQ) was found to be a transient intermediate, which was itself photolyzed largely to guanidinium nitrite. At high pH the distribution of photolysis products was different, and nitrogen gas was formed [174].

While nitrate esters in aqueous solution are not significantly photolabile, they are readily hydrolyzed at higher pHs. Because desensitization of wastewater from NG manufacture by chemical treatment with calcium hydroxide has been viewed as a viable treatment option, the kinetics and the products formed on hydrolysis of NG and each of the isomeric DNGs and MNGs were extensively studied [175-177]. The results show that chemical hydrolysis does not follow the stepwise, successively slower pathway found for microbiological systems. Rather, NG was hydrolyzed more slowly than the DNGs or MNGs to a complex mixture of products, notably nitrate, nitrite, and oxalate [177]. 1,3-DNG was hydrolyzed to glycidyl nitrate (19a), and 1,2-DNG was shown to isomerize to 1,3-DNG before hydrolysis to

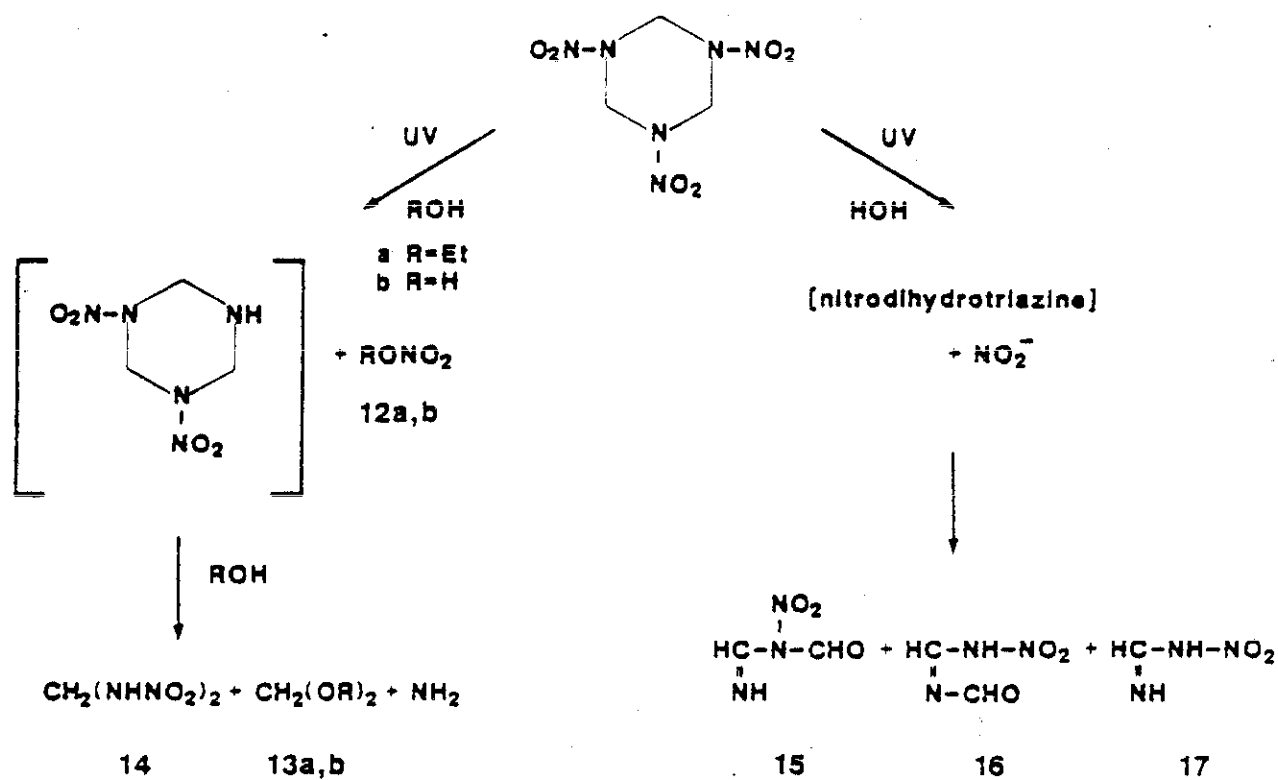


Figure 6. Photolysis Pathways of RDX

Table 5. Photolysis Products of Nitroguanidine and Nitrosoguanidine^a

Product	Reactant/Conditions			
	NQ		NSQ	
	unbuffered	pH 10	unbuffered	pH 10
NSQ				
maximum	0.02	0.008	1.00	1.00
terminal	<0.002	<0.003	ND ^b	ND
Guanidine	0.37	0.05	0.90	0.15
Cyanoguanidine	0.05	0.015	0.03	0.01
Urea	0.29	0.19	NM ^c	0.22
Nitrite N	1.10	0.65	1.4	0.9
Nitrate N	0.17	ND	ND	ND
Ammonia N	0.10	NM	0.06	NM
Nitrogen gas ^d	ND	0.23	NM	NM

a. Quantities are expressed as mole product/mole reactant; except where noted, initial reactant concentrations were $0.5-1 \times 10^{-3}$ M.

b. Not detected.

c. Not measured.

d. Initial reactant concentrations were 10^{-2} M.

the same product [176]. Similarly, 2-MNG was isomerized to 1-MNG before hydrolysis; the only product isolated was nitrate. Glycidol (19b) was isolated only on brief treatment of 2-MNG with 30% sodium hydroxide [175]. In every case the calcium hydroxide hydrolyses were kinetically second order (or pseudo-first order with excess hydroxide). The chemically generated epoxides 19a,b were found to be biodegradable [178].

METABOLISM

In mammalian systems the principal metabolites of TNT are 2-amino-4,6-DNT (2ADNT) and 4-amino-2,6-DNT (4ADNT); smaller amounts of 2,4-diamino-6-nitrotoluene and trace amounts of 2,6-diamino-4-nitrotoluene are also formed. This pattern has been found repeatedly in urine of rats, blood of rabbits, and urine of munitions workers [179,180]. In one reported plant metabolism study 4ADNT and, to a lesser extent, 2ADNT were found throughout the plant [181]. We have estimated first order rate constants for clearance of ¹⁴C-TNT in 4 mammalian species based on data for tissue distribution and excretion of the radiolabel [182]; the half-lives therefrom were 4-7 hours.

Clinical investigations of NG have shown that the major metabolites are 1,2- and 1,3-DNG; recent procedures for their determination in picogram amounts from blood plasma have been published [183-185]. Because both TNT and NG are readily absorbed through the skin, analysis of metabolites may be a promising forensic tool [179,186].

Studies of 2,4- and 2,6-DNT in rats [187,188] and in humans [189,190] show that reduction of the nitro groups is not the predominant metabolic pathway for either isomer; rather, oxidation of the methyl group is favored. For 2,4-DNT in both species, 2,4-dinitrobenzoic acid (DNBA) is the major metabolite. In rats, 2,4-dinitrobenzyl alcohol (DNBalc, excreted as glucuronide) predominated over 2-amino-4-nitrobenzoic acid (7b) [188], while in humans the reverse was observed. For 2,6-DNT in rats, a roughly 1:1:1 mixture of the three corresponding metabolites resulted [187], whereas in humans roughly equal amounts of DNBA and DNBalc were found and 2-amino-6-nitrobenzoic acid was not detected.

In rats ^{14}C -RDX was metabolized in the liver; after 4 days 40-50% of the label was recovered as CO_2 and up to 35% was found in the urine, largely as unidentified metabolites [191,192]. Only 10% of the label remained in the carcass. Estimates of clearance rates from these data resulted in half-lives of 24-30 hours. In one recent case of human ingestion [193] the question of metabolism was not addressed, but quantitative HPLC determinations showed maximum RDX concentrations of 11 mg/L in the serum after 24 hours, and 38 mg/L in the urine after 48 hours [194].

In rats ^{14}C -NQ was not metabolized but was quantitatively recovered unchanged in the urine [195]. The exceedingly low acute toxicity of the compound (Table 6) is in accord with this observation.

In humans and animals the major metabolite of PA has long been known to be picramic acid (2-amino-4,6-dinitrophenol, PrA). The metabolism of each of these compounds has recently been studied in rainbow trout [79]. In separate experiments, PA was reduced to PrA and PrA was oxidized to PA, and in both cases mixtures of the two glucuronides were obtained. Bioconcentration factors (BCF) of <1 for both PA and PrA in trout epaxial tissue were determined in this study, and may be attributed to facile conjugation and excretion.

MAMMALIAN TOXICOLOGY (INCLUDING HUMAN)

The effects of nitrate esters (notably NG, EGDN, PGDN, and PETN) on human and animal health and physiology have long been known and are detailed in a recent comprehensive review [196]. In humans, the most prominent manifestations of NG and EGDN toxicity are severe headaches and adverse cardiovascular effects. PGDN at levels twice that of the recommended threshold limit value (TLV) (see Table 11) causes headache, but no cardiovascular or neurological effects were found in studies of occupationally exposed torpedo maintenance workers [196-198]. Data are sparse for PETN, but it appears to be relatively non-toxic [196].

Toxic manifestations of TNT in humans, notably aplastic anemia and toxic hepatitis, have been known for at least 70 years, and similar conditions have been observed in animals [199,200]. Other related nitroaromatics (DNT, DNB, PA, and tetryl) produce similar effects at high doses; PA and tetryl also cause contact dermatitis [199]. Little information is available for TNB.

RDX has adverse effects on the central nervous system (CNS) in mammals [201,202], and produces convulsions and/or unconsciousness on exposure by inhalation or by ingestion [193,203-205]. In cases of human intoxication, recoveries have been complete within days or, at worst, several months after exposure. Medical evaluation of workers chronically exposed to RDX at low levels (not greater than 1.57 mg/m³) has shown no abnormalities of hematologic, hepatic, or renal systems [206]. Similar CNS effects have been demonstrated for HMX in rodents, but at significantly higher doses [207]. NQ has not been found significantly toxic to rodents [208-210].

Acute toxicities to rodents are summarized in Table 6, and Table 7 summarizes the no-observed-effect-levels (NOEL) estimated from certain of the longer term chronic and sub-chronic studies.

Evidence for carcinogenicity of TNT and RDX from mammalian studies is limited; consequently both compounds have been classified by the U.S. Environmental Protection Agency (EPA) as class C carcinogens (see Table 11). DNT, on the other hand, is well recognized as carcinogenic to rodents. Because much of the mammalian toxicity testing of DNT has been carried out on mixtures of the 2,4- and 2,6-isomers, there has been considerable confusion as to the roles of the individual isomers in carcinogenesis. Recent work, however, has established that in rats 2,6-DNT appears to be a complete hepatocarcinogen (initiator and promotor), while 2,4-DNT is an apparent pure promotor and is considered a much less potent carcinogen [211].

As to the question of carcinogenicity of DNT in man, the results of a recent retrospective cohort mortality study involving 457 former personnel occupationally exposed to DNT at Joliet and Radford Army ammunition plants during the 1940s and 1950s provide some significant information [212]. Workers at Joliet were exposed to crude DNT (containing 19% 2,6-isomer) while at Radford the DNT contained no more than 1% 2,6-isomer. No deaths from any type of cancer in excess of the "standard mortality ratio" or percentage of expected deaths were found in either of the two groups. On the other hand, elevated mortality due largely to heart and circulatory diseases of atherosclerotic origin was found in both groups. The data suggested a correlation of increased mortality with duration and intensity of exposure.

A similar mortality study involving workers occupationally exposed to TNT and EGDN in the Swedish dynamite industry showed double the expected number of deaths from cardio-cerebrovascular causes [213].

Table 6. Acute Toxicities of Munitions Compounds to Rodents

Compound	Rat mg/kg ^a (route)	Mouse mg/kg ^a (route)	Reference
TNT	800-1300 (oral)	600-1000 (oral)	214
DNT	200-800 (oral)	1200-2000 (oral)	215
NG	500-900 (oral)	500-1200 (oral)	216
	100-110 (ip)	100-200 (ip)	216
	25-32 (iv)	10-18 (iv)	216
	500-600 (sc)	30-500 (sc)	216
RDX	40-300 (oral)	60-500 (oral)	201
		19 (iv)	201
HMX	6250 (oral)	2300 (oral)	217
		634 (sc) ^b	207
NQ	>5000 (oral)	5000 (oral)	195, 208, 209
TNB	450 (oral)	572 (oral)	63
		32 (iv)	63
DNB	83 (oral)	200 (ip) ^c	63
DEGDN	700-1000 (oral) ^d	1300-1400 (oral) ^d	218
	777 (oral)		63
EGDN	616 (oral)		63
PGDN	250 (oral)		63
	479 (ip)	1047 (ip)	63
	463 (sc)	1208 (sc)	63
PA		100 (oral) ^e	63
Tetryl		5000 (sc) ^f	63

a. LD50 unless noted otherwise.

b. In rabbit.

c. LDLo.

d. LD100.

e. LDLo in guinea pig.

f. LDLo in dog.

Table 7. NOEL for Selected Munitions Compounds Estimated from Chronic and Subchronic Toxicity Data

Compound	Duration of Test	NOEL (mg/kg/day)	Species	Reference
TNT	13 wk	1.0 ^a	rat	219
	13 wk	1.4-1.45 ^b	rat	220
	13 wk	1.45-1.6 ^{b,c}	mouse	220
	13 wk	0.2	dog	220
	26 wk	0.5 ^d	dog	221
	2 yr	0.4	rat	222
DNT	1 yr	13.5	mouse	223,224
	1-2 yr	0.6	rat	223,225
	2 yr	0.2	dog	223
NG	13 wk	25.5	rat	226
	1 yr	1.0	dog	227
	2 yr	3-4 ^b	rat	227
	2 yr	10-11 ^b	mouse	227
RDX	13 wk	15	rat	202
	13 wk	80	mouse	202
	13 wk	1.0	monkey	202
	2 yr	0.3	rat	228
	2 yr	1.5	mouse	229
HMX	13 wk	50-115	rat	207
PA	2 yr	25 ^e	rat	230
NQ	13 wk	316	rat	210
DNB	16 wk	0.75	rat	231,232
PETN	1 yr	2	rat	196

a. 5% reduction in weight gain.

b. Males and females were given slightly different doses.

c. Enlarged spleens and hearts.

d. Mild liver lesions observed in 7 of 12.

e. Calculated from concentration in feed (500 ppm), assuming standard animal weight (200 g) and feed consumption (10 g/day)[63].

AQUATIC TOXICOLOGY

TNT, DNT, and the many other nitroaromatic by-products of TNT manufacture have been extensively investigated both singly and in mixtures. Acute studies utilized a variety of fish, invertebrate, and algal species [233-235], and the test conditions (static or flow-through), concentration determinations (nominal or measured), and biological endpoints were not generally uniform. Endpoints were usually determined as 48- and 96-hour LC50s, or as time-independent concentrations termed as "incipient" LC50s and defined as the concentration above which 50 percent of the test organisms would not survive indefinitely [236]. Table 8 summarizes the results of acute toxicity tests conducted under static conditions for a variety of fish and invertebrates, and Table 9 is a similar summary of tests conducted under flow-through conditions and including incipient as well as time-dependent LC50 determinations.

Comparison of the 96-hr LC50s for the four fish species shows significantly lower values for the flow-through conditions, except in the bluegill case. In general under the flow-through conditions, incipient LC50s were consistently lower than the 96-hr values. For the fish, it is apparent that photolysis reduced toxicity in the static tests. Variation of water quality parameters such as hardness, pH, and temperature had little effect on acute toxicities of TNT [234].

The various nitroaromatics resulting from the TNT manufacturing process have been tested, both as individual compounds and in mixtures of condensate water (p.18), for acute toxicity to fathead minnows and water fleas [233]. The results for selected compounds are summarized in Table 10. It is evident that 2,4- and 2,6-DNT, the most abundant constituents of condensate water, are among the least toxic. The table further shows a remarkable correlation of substitution pattern with toxicity among the DNT isomers. Isomers with ortho (2,3 and 3,4) and para (2,5) nitro groups are about 10-20 times more toxic than those with meta (2,4, 2,6, and 3,5) nitro groups. This effect is also manifest to an even greater degree in the comparative toxicities of 2,3,6- and 2,4,6-TNT. The somewhat greater toxicities observed for condensate water relative to its major constituent are readily attributable to the presence of these highly toxic minor components.

Full life-cycle chronic tests have been made with fathead minnows and water fleas for TNT, DNT, and condensate water [237,238]. Early life stage tests (30, 60, and 90 days) were made with fathead minnows, channel catfish, and rainbow trout. Reproductive parameters included spawning, egg hatching, and fry survival and growth. Results of the chronic studies showed adverse effects even at the lowest concentrations tested (0.04 mg/L for TNT and 0.28 mg/L for DNT). In three-generation tests with fathead minnows, adverse effects were generally more pronounced in the later generations. In the early life stage tests substantially higher concentrations were required for observation of adverse effects.

Most of the available information on toxicity of TNT (and in a few cases, DNT) to aquatic plants deals with algal species exposed from 16 hours [239] to 15-17 days [240]. Concentrations at least as high as the incipient LC50s observed for fish and water fleas (Table 9) were required for adverse effects. One study reported a value of 1.0 mg/L for growth inhibition of the vascular species Lemna perpusilla (duckweed), and death of the plant at 5 mg/L [241]. Only a single study of the effect of TNT on the growth of a terrestrial plant, yellow nutsedge

Table 8. Acute Toxicity of TNT to Selected Species of Fish and Invertebrates under Static Conditions^a

Species	Exposure Time (hr)	LC50 (mg/L) ^b	
		non-photolyzed	photolyzed ^c
Fathead minnow (<i>Pimephales promelas</i>)	96	2.9 (2.6-3.2)	12.8 (11.6-13.9)
Channel catfish (<i>Ictalurus punctatus</i>)	96	2.4 (2.0-2.7)	5.5 (4.8-6.4)
Rainbow trout (<i>Salmo gairdneri</i>)	96	0.8 (0.7-1.0) 1.4 (1.2-1.8) ^d	13.9 (9.0-18.0)
Bluegill (<i>Lepomis macrochirus</i>)	96	2.6 (2.3-2.9) 3.4 (3.1-3.7) ^d	18.3 (17.2-19.5)
Water flea (<i>Daphnia magna</i>)	48	11.7 (10.9-12.6)	16.5 (14.3-18.6)
Scud (<i>Hyalella azteca</i>)	48	6.5 (5.6-7.5)	6.7 (5.0-8.9)
Midge (<i>Tanytarsus dissimilis</i>)	48	27.0 (22.0-33.0)	25.2 (17.3-30.6)
Earthworm (<i>Lumbriculus variegatus</i>)	48	5.2 (4.5-6.0)	19.2 (16.0-22.3)

a. Data from reference 234. Concentrations nominal.

b. Data in parentheses represent 95% confidence limits.

c. LC50s for photolyzed TNT are based upon conc of TNT before irradiation with a Pyrex-filtered medium pressure mercury lamp.

d. Test solutions aerated.

Table 9. Acute Toxicity of TNT to Selected Species of Fish and Invertebrates under Flow-through Conditions^a

Species	LC50 (mg/L)			
	48-hr	96-hr	Incipient ^b	Duration (hr)
Fathead minnow	5.9	3.7	1.5 (0.9-2.5)	384
Channel catfish	5.6	3.3	1.6 (0.9-3.0)	288
Rainbow trout	2.0	2.0	1.9 (1.3-3.3)	240
Bluegill	2.6	2.5	1.4 (0.8-2.5)	312
Water flea	>4.4	1.2	0.2 (0.1-1.0)	192
Earthworm	>29.0	>29.0	13.9 (12.6-15.1)	336

a. Data from reference 234. Concentrations measured.

b. Data in parentheses represent 95% confidence limits.

Table 10. Acute Toxicity of Selected Constituents of Condensate Water to Fathead Minnows and Water Fleas under Static Conditions^a

Compound ^b	Fathead minnow	Water flea
	96 hr LC50 (mg/L) ^c	48 hr LC50 (mg/L) ^c
2,4-DNT	32.8 (27.3-38.0)	47.5 (29.5-99.7)
2,6-DNT	18.5 (17.2-20.2)	21.8 (19.3-24.6)
1,3-DNB	7.0 (5.8-8.1)	49.6 (42.5-59.2)
	16.8 ^d	27.4 (24.0-31.4) ^d
3,5-DNT	22.6 (13.4-27.1)	45.2 (42.4-48.4)
3,4-DNT	1.5 (1.1-1.8)	3.7 (1.0-5.4)
2,3-DNT	1.8 (1.5-2.1)	4.7 (3.0-5.9)
2,5-DNT	1.3 (1.1-1.4)	3.1 (2.2-3.8)
2,4,6-TNT	2.9 (2.6-3.2)	11.7 (10.9-12.6)
2,3,6-TNT	0.1 (0.10-0.13)	0.8 (0.4-1.2)
1,3,5-TNB	1.1 (1.0-1.2)	2.7 (2.4-3.1)
	0.5 (0.4-0.6) ^d	3.0 (2.6-3.4) ^d
3,5-Dinitroaniline	21.8 (19.1-31.3)	15.4 (13.5-18.0)
	21.2 (15.1-29.9) ^d	13.8 (12.9-14.8) ^d
2-Amino-3,6-DNT	0.9 (0.7-1.2)	2.5 (0.7-6.5)
3-Amino-2,4-DNT	12.2 (10.8-13.4)	9.6 (5.5-11.0)
Condensate water	185 (164-207)	

- a. Data from reference 233 unless noted otherwise. Concentrations nominal.
b. Listed in order of decreasing occurrence in condensate water; the first 3 constitute 43%, 22%, and 12%, respectively, of the total organic content.
c. Data in parentheses represent 95% confidence limits.
d. Data from reference 235.

(*Cyperus esculentus* L.), in hydroponic culture has been published [181]. Adverse effects were observed at 5 mg/L, the lowest concentration studied.

Information regarding adverse effects of RDX to aquatic organisms is sparse. One study cited 96-hr LC50s of 4-6 mg/L (static) and 7-13 mg/L (flow-through), and incipient LC50s of 5-11 mg/L (flow-through) in the four fish species listed above (Tables 8,9) [242]. The validity of these and other data reported in the study has been questioned [201,243]. Acute toxicities of mixtures of RDX and TNT (1.6:1) were not significantly different from those observed for TNT alone [234]. No toxic effects were observed for HMX up to its solubility limit (5 mg/L).

NQ is essentially non-toxic to aquatic organisms [244]. Acute tests with four fish species and five invertebrates showed no LC50s up to the solubility limits (ranging from 1.7 to 3.0 g/L at temperatures between 12 and 22°C). Chronic toxicity was also exceedingly low. A 42-day early life stage test with rainbow trout (the species found most sensitive) showed significant differences from the controls only at saturation. The mixture produced by photolysis of NQ, however, was about 100 times more toxic to fathead minnows and water fleas (LC50 and EC50 about 30 mg/L in each case). Of the major NQ photolysis products (Table 5), guanidine and/or nitrite may account for the observed toxicities.

NG, on the other hand, is quite toxic to fish, with 96-hr acute (both static and flow-through) values of 1.7-4 mg/L for four species. Chronic studies in the fathead minnow showed adverse effects from as little as 0.2 mg/L. Four species of invertebrates were less sensitive, with 48 hour EC50s in the range 20-55 mg/L [77].

An acute toxicity study of DEGDN to four species of fish and four species of invertebrates showed it to be relatively non-toxic [245]. The most sensitive invertebrate (water flea) was substantially more sensitive (48-hr EC50 90 mg/L) than the most sensitive fish (96-hr static LC50 258 mg/L, bluegill).

Acute toxicities (96-hr LC50) of 110 and 46 mg/L for PA and picramide, respectively, to rainbow trout have been reported [246]. A 42-day chronic study in rainbow trout at concentrations <0.001 LC50 of PA and picramide showed no growth inhibition, but in both cases >80% of the fish developed petechial lesions [247]. Similar 42-day studies with PA and picramic acid concentrations as low as 0.05 and 0.02 mg/L, respectively, showed significant uptake and inhibition of growth in oysters (*Crassostrea virginica*) [247,248].

While insufficient toxicological data are available at present to meet the most recent EPA guidelines [249] for numerical estimates of water quality criteria to assure protection of the aquatic biota, some interim estimates have been made on the basis of the available data for selected munitions compounds. The criteria specify two concentrations, a criterion maximum concentration (CMC) and a criterion continuous concentration (CCC), which should not be exceeded. Estimated values for TNT were, respectively, 0.56 and 0.04 mg/L [214]; for DNT, 5.5 and 0.2 mg/L [215]; and for NG 0.86 mg/L (CMC only) [216].

WATER QUALITY CRITERIA AND STANDARDS FOR HUMAN EXPOSURE

The ultimate products of mammalian toxicological evaluation and human epidemiology of environmental pollutants are official opinions, criteria, or standards for human exposure. Such regulatory or quasi-regulatory values have been developed in the U.S. for ten of the compounds discussed above (Table 11).

Threshold limit values (TLV) have been issued by the American Conference of Industrial Hygienists as recommended occupational health standards; TLVs have generally been accepted as permissible exposure limits (PEL) by the U.S. Occupational Safety and Health Administration (OSHA), though often after lag times of several years.

The EPA Office of Drinking Water (ODW) publishes health advisories (HAs) that are not binding according to federal law; nevertheless individual states have included values from HAs in their regulations as if such numbers had been fully validated. The drinking water equivalent levels (DWEL) cited by ODW in HAs (Table 11) are based on the assumptions of non-carcinogenicity of the compound and of drinking water as the sole source of human exposure. Additional safety factors are applied in the calculation of lifetime advisory limits to allow for other routes of exposure and for the uncertainty as to the no-effect level of compounds designated by EPA as class C carcinogens (see Table 11) [202,226,250].

It must be emphasized, in conclusion, that both our understanding of the toxicology of environmental pollutants and the application or conversion of toxicological data to criteria for decision making are still in the early stages of development.

Table 11. Proposed and Official Regulatory Values and Classifications

Compound	ACGIH TLV ^a		OSHA/NIOSH PEL/REL ^b			HA DWEL ^e mg/L	Potency factor ^f (mg/kg/d) ⁻¹	Carcinogen class ^h
	ppm ^g	mg/m ³	TWA ^c ppm ^g	mg/m ³	STEL ^d mg/m ³			
TNT	-	0.5	-	1.5, (0.5) ⁱ	-	0.020	0.031	C
2,4-DNT	-	1.5	1.5	-	-	-	0.311 ^j	B2
DNB	0.15	1	0.15	1	-	-	-	-
RDX	-	1.5	-	-	-	0.10	0.11	C
HMX	-	-	-	-	-	1.8	-	D
Tetryl	-	1.5	-	-	-	-	-	-
PA	-	0.1	-	0.1	0.3	-	-	-
NG	0.05	0.5	0.2	2	(0.1) ^k	0.005	0.0166	-
EGDN	0.05	0.3	0.2	1	(0.1) ^k	-	-	-
PGDN	0.05	0.3	-	-	-	-	-	-

- a. American Conference of Governmental Industrial Hygienists threshold limit value [251].
- b. Occupational Safety and Health Administration (OSHA) permissible exposure limit and National Institute of Occupational Safety and Health (NIOSH) recommended exposure limit [252].
- c. Time weighted average for an 8-hr/day, 5-day workweek [251].
- d. Short-term exposure limit, usually 15 min, not to be repeated more than 4 times per day or at intervals of <60 min [251].
- e. EPA Office of Drinking Water (ODW) drinking water equivalent level for lifetime exposure. DWELs have been published in the respective Health Advisories (HAs) [202,207,226,250].
- f. Carcinogenic potency factor, q_1^* , calculated by ODW. Multiplying q_1^* in (mg/kg/day)⁻¹ by the daily exposure level in mg/kg/day gives the lifetime cancer risk, R. Thus if one assumes an acceptable R of 10^{-6} (one excess cancer from a lifetime exposure of one million people), an acceptable daily exposure level is $10^{-6}/q_1^*$ mg/kg. Unless otherwise noted, values appear in the respective HAs [202,226,250].
- g. Parts per million in the vapor phase, i.e. molecules per million molecules of air. At 25°C, ppm = (mg/m³ x 24)/MW.
- h. Group classifications as follows have been made by USEPA.
B2: Probable human carcinogen; usually on the basis of adequate evidence in animals and inadequate evidence or insufficient data in humans.
C: Possible human carcinogen; limited evidence of carcinogenicity in animals and insufficient data in humans.
D: Not classified as carcinogen; insufficient evidence from animal studies.
- i. Currently proposed by OSHA.
- j. ODW has not yet issued HAs for 2,4- or 2,6-DNT. However, a tentative value of 0.311 (mg/kg/day)⁻¹ for the carcinogenic potency factor q_1^* for 2,4-DNT has been cited [253]. Assuming a value of 10^{-6} for R (see footnote f), the acceptable exposure limit is $10^{-6}/0.311$ or 3.2×10^{-6} mg/kg/day. Thus, for a 70 kg individual consuming 2 L of water per day, a concentration of 0.00011 mg/L is calculated.
- k. Currently recommended by NIOSH for 20-min STEL.

RECOMMENDATIONS

The following recommendations concern scientific gaps or uncertainties in the data base currently available for munitions compounds which, in the view of the authors, need to be filled or clarified in order to facilitate development of environmental control, cleanup, and monitoring policies and measures.

1. In cases where $\log K_{ow}$ has not been determined experimentally (PETN, PGDN) or where discrepancies exist between experimental values (TNT) or between experimental and calculated values (NG, EGDN), further measurements need to be made.
2. Experimental determination of $\log K_{oc}$ for many of the compounds in Table 4, in several well-characterized soils of different organic content, would be valuable.
3. Experimental determination of K_H for the more volatile compounds (DNTs, DNB, NG, EGDN, DEGDN, PGDN) would be desirable.
4. Experimental determination of BCF in bluegills or fathead minnows, especially for the compounds with the highest calculated values (PETN, PGDN), is needed.
5. Aquatic toxicity studies according to the most recent EPA-mandated protocol [247] should be completed for TNT, 2,4-DNT, NQ, and NG, and should be undertaken for the other compounds in Table 4.
6. Experimental determination of BCF and clearance time in ruminants would be desirable for TNT, the DNTs, RDX, and NG.
7. Since reduction of aromatic nitro compounds to amines takes place readily in biological and environmental systems and little is known about the stability or biodegradability of the amines, studies of their environmental and metabolic fate are recommended.

GLOSSARY

<u>Symbol</u>	<u>Definition</u>
BCF	Bioconcentration factor
ΔF_f	Free energy change in going from solid to liquid state
ΔH_m	Heat of fusion
K	Degrees Kelvin
K_H	Henry's law constant
K_d	Actual partition coefficient of a chemical between soil and water
K_{oc}	Soil organic carbon/water partition coefficient
f_{oc}	Fraction of organic carbon in soil; $f_{oc} = K_d/K_{oc}$
K_{ow} (or P_{ow})	Octanol-water partition coefficient
MW	Molecular weight
P	Vapor pressure
$P(l)$	Vapor pressure in liquid state
$P(s)$	Vapor pressure in solid state
R	Gas constant
S	Solubility in water (mg/L, unless noted otherwise)
ΔS_f	Entropy of fusion
T	Temperature in degrees Kelvin
T_m	Melting point in degrees Kelvin unless specified otherwise

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